

Modeling the Fate of Acetochlor and Terbutylazine in the Field Using the Root Zone Water Quality Model

Q. L. Ma,* A. Rahman, T. K. James, P. T. Holland, D. E. McNaughton, K. W. Rojas, and L. R. Ahuja

ABSTRACT

Data collected from a 3-yr controlled field study in Hamilton, New Zealand were used to examine whether the Root Zone Water Quality Model is capable of predicting water movement and pesticide fate in the field based on key lab-measured parameters and environmental variables. Acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide; 2.5 and 5.0 kg a.i. ha⁻¹] and terbutylazine (C₉H₁₆ClN₅; 1.5 and 3.0 kg a.i. ha⁻¹) were applied onto nine field plots (3 by 9 m each). Soil core samples were taken to a depth of 1 m to determine soil water contents and pesticide concentrations. Dissipation of both pesticides in the field at both application rates followed first-order kinetics (adjusted $r^2 > 0.91$). The mean dissipation half-life was 16 d for acetochlor and 25 d for terbutylazine. Relatively small amounts of the pesticides leached below 5 cm and none leached below 10 cm. Predicted soil water contents in the soil profile were not significantly different from those measured in the field ($p > 0.84$). Predicted acetochlor and terbutylazine masses in the soil profile based on a linear instantaneous-equilibrium (I-E) partitioning model matched those measured in the field (adjusted $r^2 > 0.93$). However, predicted pesticide concentrations in the soil profile were less satisfactory, with 68 and 35% of the predicted concentrations being within a factor of 2 of the measured concentrations for 0- to 5- and 5- to 10-cm depths, respectively. Calibration of each pesticide sensitive parameter individually did not significantly improve the overall predictions of pesticide mass and concentrations in the soil profile when the I-E partitioning model was used. The predictions were improved when a two-site, equilibrium-kinetic (E-K) sorption model was used.

THE CONCENTRATION and persistence of pesticide residues in soils have both economical and environmental significance and are often used as key indicators for environmental risk assessments. Therefore, significant research efforts have been directed to the development of effective tools for predicting pesticide concentration and persistence in the field. Simulation models have been developed that integrate pesticide properties, soil properties, climatic conditions, and management practices for such predictions. The hypothesis is that adequate predictions of pesticide fate in the field can be approached with these simulation models using key parameters measured in the lab coupled with measured environmental variables.

Walker (1974) predicted pesticide persistence in the field using parameters primarily derived from the lab

incubation studies. Although Walker's model was generally found to overestimate total soil residues at later sampling dates (Walker, 1987), Heiermann et al. (1995) reported that this model greatly underestimated the persistence of two pesticides during cold, wet seasons in a Germany site. This suggests that the model's performance is significantly affected by site-specific soil and environmental conditions.

A simple model, such as that developed by Walker (1974), has the advantages of easy operation and application. The most obvious disadvantage is the difficulty for the users to explore the effects of various factors on model simulations as these factors are frequently lumped. Moreover, the model was specifically designed only for predicting pesticide persistence in the field. The need for accurate predictions of pesticide concentration and persistence from chemical and physical processes has encouraged the development of more complex models for simulating pesticide fate and transport in soils. GLEAMS (Leonard et al., 1987), LEACHM (Wagenet and Hutson, 1987), MACRO (Jarvis, 1994), PRZM (Carsel et al., 1998), and RZWQM (Ahuja et al., 2000) are among the recently developed process-based models. They were developed in response to the demand for models with relatively high scientific credibility. RZWQM is one of the latest developed numerical models that incorporate detailed processes for simulating soil-water movement and pesticide dissipation and transport in agricultural systems. Furthermore, RZWQM has a user-friendly, Microsoft Windows (Microsoft Inc., Redmond, WA) based interface that greatly enhances model parameterization and operations. In particular, the pesticide submodel incorporates some of the findings and recommendations of the FOCUS and FIFRA modeling workshops (Wauchope et al., 2000). The hypothesis that process-based models should deliver better accuracy in model predictions, especially with enhanced model parameterization, seems to be supported by recent validation studies with RZWQM (Ma et al., 1995; Singh and Kanwar, 1995; Ahuja et al., 1996) and other models (Pennell et al., 1990).

A simulation model such as RZWQM has to be thoroughly tested under local conditions before using as a management and analytical tool for local government and regulatory agencies. This is because of the site-specific nature of simulation models. However, it has been frequently not possible to obtain suitably comprehensive data for validating all processes and state vari-

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Abbreviations: E-K, equilibrium-kinetic; FIFRA, Federal Insecticide, Fungicide and Rodenticide Act; FOCUS, Forum for the coordination of pesticide fate models and their uses; HPLC, high-pressure liquid chromatography; I-E, instantaneous equilibrium; MWHC, maximum water holding capacity; NRMSE, normalized root mean square error; OECD, Organization for Economic Co-operation and Development.

ables, even though great detail may have been available on selected variables and processes. An alternate, attainable step toward ultimate model validation may be to test part of the model at a time and progressively gain confidence by extending the tests with more data.

New Zealand has distinct weather conditions and soil properties. In particular, the Waikato region has high solar radiation and frequent rainfall all year round and volcanic soils of high organic C content and low bulk density that provide a unique scenario for RZWQM to simulate. The interest of local regulatory agencies in the model also promoted this study. Therefore, the objectives were (i) to investigate persistence and leaching of acetochlor and terbuthylazine in New Zealand soil and weather conditions; and (ii) to evaluate the capability of RZWQM to predict water movement and pesticide fate in the field based on lab-measured parameters and environmental variables with and without further model calibration. Acetochlor and terbuthylazine were selected because they have been widely used in New Zealand and concerns have been raised regarding their potential risks to water quality and human health. They were selected also because of the perceived long persistence of the pesticides in soils.

MODEL DESCRIPTION

RZWQM (98-1.0-2001, October 2001) is a one-dimensional, numerical model for simulating the vertical flow of soil water and solutes in the saturated and unsaturated crop root zone. Ahuja et al. (2000) gave a thorough description of RZWQM. The following is a brief description of the major algorithms used to simulate water movement and pesticide fate and transport in soils.

Hydrology Submodel

A two-domain water flow model is used in RZWQM, where the two domains are soil matrix and macropores. Water infiltration into soil matrix during rainfall and irrigation is described by a modification of the Green-Ampt equation (Ahuja et al., 2000). When rainfall rate exceeds infiltration rate, surface runoff is produced, which also triggers macropore flow. Redistribution of water in the soil matrix following infiltration is modeled by a mass-conservative numerical solution of the Richards' equation (Celia et al., 1990):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(h, z) \frac{\partial h}{\partial z} - K(h, z) \right] - S(z, t) \quad [1]$$

where θ is soil water content, K is hydraulic conductivity, both are functions of soil water potential h , depth z , and time t ; $S(z, t)$ is a sink term for plant root water uptake and tile drain rate. The $S(z, t)$ term is solved following Nimah and Hanks (1973). The soil water retention and hydraulic conductivity functions [$\theta(h)$ and $K(h)$ functions] in Eq. [1] are described by a modification of the Brooks and Corey function (Ahuja et al., 2000).

RZWQM uses a modification of the double-layer Penman-Monteith type model (Farahani and Bausch, 1995) to calculate potential soil evaporation and crop transpiration. A generic plant growth model is used to simulate plant growth and phenology in RZWQM (Hanson, 2000).

Pesticide Submodel

To reflect the distinctive behaviors of pesticides in different compartments of an agricultural system, the system is conceptually divided into four compartments (Wauchope et al., 2000): crop foliage, crop residue, soil surface, and soil subsurface or root zone. Degradation of pesticides in each compartment is assumed to follow a pseudo first-order kinetics:

$$C = C_0 \exp(-kt) \quad [2]$$

where C_0 is initial pesticide concentration; C is pesticide concentration on Day t ; and k is a pseudo first-order rate constant. The values of k for soil surface and subsurface compartments are adjusted for temperature and soil water content as described by Walker (1974) and Walker et al. (1996):

$$k(T, \theta) = k(T_{ref}, \theta_{ref}) \exp \left[\frac{E_a}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \left(\frac{\theta}{\theta_{ref}} \right)^{-\beta} \quad [3]$$

where $k(T, \theta)$ is the rate constant at temperature T (K) and soil water content θ ; $k(T_{ref}, \theta_{ref})$ is rate constant at reference temperature T_{ref} (K) and reference soil water content θ_{ref} ; E_a is degradation activation energy; R is the universal gas constant; and β is Walker's constant. Pesticide dissipation pathways in soils can include volatilization, photolysis, abiotic, aerobic, and anaerobic degradation. Volatilization and photolysis can occur only in the soil surface compartment (0–1 cm), while the anaerobic degradation can occur only in the soil subsurface compartment. In addition, RZWQM assumes the user-input degradation half-life applies for the top 25-cm layer and then it decreases linearly from 25 to 75 cm. Degradation half-life below 75 cm is set equal to that at 75 cm.

Adsorption of pesticides in soils can be simulated by a linear I-E partitioning model, a nonlinear Freundlich adsorption model, or a two-site, equilibrium-kinetic (E-K) sorption model (Ma et al., 1996; Wauchope et al., 2000). The E-K sorption model assumes that pesticide sorption on a fraction (F) of the sites is instantaneous, whereas sorption on the remainder of the sites ($1-F$) is time-dependent, described by a first-order reversible kinetics (Ma et al., 1996):

$$\frac{dC_a}{dt} = RK_2(EK_2 C_1 - C_a) = RK_2[(1-F)K_d C_1 - C_a] \quad [4]$$

where C_1 and C_a are pesticide concentrations in soil solution and on kinetic sorption sites, respectively; RK_2 and EK_2 are reversible kinetic and kinetic sorption rate constants, respectively. The I-E adsorption model is used in the uncalibrated mode, while the E-K sorption model is used in the calibrated mode of this study when the I-E adsorption model fails to adequately describe pesticide adsorption.

Transfer of pesticides from soil to surface runoff is simulated by a nonuniform mixing model (Heathman et al., 1986), which assumes that pesticides in the top 2-cm of the soil are subject to runoff. Mass transfer of pesticides between soil layers is modeled on the basis of the contemporary miscible displacement theory with a partial-piston displacement and partial-mixing for each 1-cm depth increment (Ahuja et al., 2000). Pesticide displacement and mixing occur only in mesopores and macropores (mobile phase). But pesticide diffusion is allowed between micropores (immobile phase) and mesopores according to Fick's first law. The mesopore and micropore regions are defined either by the users or on partitioning of water retention curve at 200-kPa suction. Pesticide concentrations in both micropores and mesopores are allowed to equilibrate at the end of each time step.

A similar partial-displacement and mixing approach is used for simulating soil heat transport during a rainfall event,

whereas heat transport between rainfall events is simulated by the convection-diffusion equation that is solved by a fully implicit finite-difference scheme (Flerchinger et al., 2000). Soil profile temperatures are calculated from soil surface temperature, user-input initial soil profile temperatures, soil thermal conductivity, and heat capacity. Soil surface temperature (upper boundary temperature) is estimated using an energy balance procedure (van Bavel and Hillel, 1976). Soil thermal properties can be user-input or calculated from the basic soil physical properties using the procedure of de Vries (1963).

MATERIALS AND METHODS

Field Experiment

Nine field plots (3 by 9 m each) were established in a cultivated field (about 1 ha) (Fig. 1) of a Hamilton clay loam (Humic Hapludull, illuvial spadic) in Hamilton, New Zealand. This field had been planted to maize (*Zea mays* L.) in previous years. On 20 Nov. 1997, acetochlor (Roustabout, Monsanto [NZ] LTD, Wellington, New Zealand, 2.5 and 5.0 kg a.i. ha⁻¹) and terbuthylazine (Gardoprim, Novartis Crop Protection, Auckland, NZ, 1.5 and 3.0 kg a.i. ha⁻¹) were applied in 300 L of water per hectare to the soil surface. The lower application rates were recommended field application rates, while the higher application rates were to simulate field conditions of overlap application or excessive application of the pesticides. Applications were made by hand with a CO₂-powered sprayer using TeeJet 8003 nozzles at 200-kPa pressure. Three replicates were used for each application rate/pesticide combination in a randomized block layout (Fig. 1). All plots were kept fallow during the study by applying glyphosate [N-(phosphonomethyl) glycine] to emergent plants.

Duplicate soil cores were taken to a depth of 10 cm from each plot using a 7.5-cm diameter stainless-steel soil sampling tube, on the day of treatment and at 7, 14, 21, and 28 d after the treatment. At 41, 55, 84, 117, 147, 196, 288, 341, and 476 d after the treatment, three soil cores were taken from each plot to a depth of 100 cm using a specially designed soil sampler (Humax, Switzerland). The sampler consists of a 100-cm long stainless-steel outer tube with a 25-cm long inner tube holding a PVC casing in which the soil sample is collected. Sampling to 100-cm depth was achieved by taking four consecutive 25-cm segments. The soil samples were immediately frozen and then cut into 5-cm sections. In preparation for analysis, the core samples were partly thawed and the outside 2 to 3 mm was removed and discarded to reduce cross-contamination. This remaining sample was thawed, bulked with other samples at the same depth collected from the same plot, thoroughly mixed, and passed through a 4-mm sieve. Subsamples were used for determining soil-water content and acetochlor and terbuthylazine concentrations.

Lab Experiment

Incubation Studies

An aqueous solution (1.0 mL) of the formulated product (Gardoprim) was fortified in the soil (equivalent to 50.0 g dry weight) in flasks (250 mL) to make it equivalent to 3.0 kg a.i. ha⁻¹. The flasks were maintained at 10, 22, and 30°C at 60% maximum water holding capacity (MWHC) and at 40 and 80% MWHC at 22°C. Water was added once a week to bring the flasks up to the predetermined weight. Two flasks were taken from each combination of soil moisture and temperature at designated times for determining terbuthylazine concentrations. Incubation study was not conducted for acetochlor in this soil. However, it was conducted under the same conditions

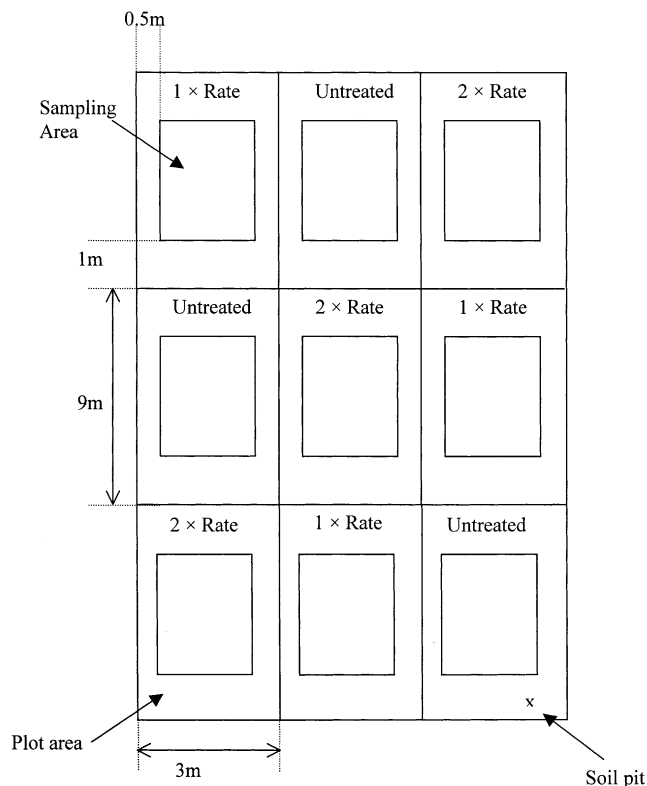


Fig. 1. Experiment layout of the field study.

for a Horotiu sandy loam soil (Typic Orthic Allophanic) at 5.0 kg a.i. ha⁻¹ rate and the derived first-order rate constants were used to predict acetochlor fate in the field. Because differences exist between these two soils, using rate constant derived from the Horotiu soil for predicting acetochlor behavior in the Hamilton soil may cause errors, as discussed later.

Equilibrium Adsorption Measurements

A modification of the standard procedure of the Organization for Economic Cooperation and Development (OECD) (OECD, 1990) was used for determining the equilibrium adsorption constants of the pesticides. Aqueous solutions (4.0 mL each) of the formulated pesticides (equivalent to twice the recommended application rate) were added to the moist soil (equivalent to 50.0 g dry weight) in flasks (250 mL). The flasks were sealed with parafilm and stored at 4°C in dark for 24 h. Soil in a set of four flasks was extracted, each with 100.0 mL of methanol/water (70/30, v/v), for 1 h on an orbital shaker (230 rpm) to obtain the total pesticide concentration. Soil in another set of four flasks was extracted, each with 100.0 mL of 0.2 M CaCl₂ solution, to obtain the aqueous concentration. The equilibrium adsorption coefficient (K_d) was calculated as the ratio of adsorbed concentration to aqueous concentration.

Pesticide Extraction and Analysis

All soil samples (equivalent to 50.0 g dry weight) for acetochlor and terbuthylazine analyses were shaken with 100.0 mL of methanol/water solution (70/30, v/v) in flasks (250 mL) for 1 h and then allowed to stand for 1 h. An aliquot of 10.0 mL of the supernatant was extracted three times with dichloromethane (7.0, 3.5 × 2 mL). The combined extracts were slowly evaporated under N₂ until dry then redissolved in 1.0 mL of methanol/water (equal volume) solution for analysis by high pressure liquid chromatography (HPLC) with an ultraviolet

(UV) detector at 230 nm. The column was Prodigy (150 × 4.6 mm) packed with 5-μm octadecylsilane (ODS)(3) held at 35°C (Phenomenex, Torrence, CA). The mobile phase was 56:44 methanol/water at a flow rate of 60.0 mL h⁻¹. This analytical procedure gave a recovery of 89 ± 14% for acetochlor and 98 ± 9% for terbuthylazine for a range of spiked concentrations from 200 to 4000 μg kg⁻¹. The analytical detection limit was 40 μg kg⁻¹ for acetochlor and 15 μg kg⁻¹ for terbuthylazine. The mean recovery was used to correct pesticide concentrations in the field.

Measurements of Soil Properties and Soil Temperature

A 120-cm deep pit was dug near an untreated plot at the experimental site (Fig. 1). Six undisturbed soil cores were collected from each of the upper five major soil horizons using stainless steel cylinders (7.6-cm height by 9.84-cm i.d.). These core samples were then used for determining saturated hydraulic conductivity (K_s) and soil water retention curves. The K_s was measured using the constant head method of Klute and Dirksen (1986). After K_s measurement, the core samples were mounted in Tempe cells and water contents were measured gravimetrically at 2.5-, 5.0-, 10.0-, 20.0-, 40.0-, and 100-kPa suctions. Water content at 1500-kPa suction was determined in a high-pressure chamber using additional loose soil from respective soil horizons. Undisturbed soil core samples were then used for determining soil bulk density. Soil particle density was determined using a pycnometer and 50.0 g of air-dry soil. Soil particle-size distribution was determined by the hydrometer method (Day, 1965). Soil organic C content was determined by the Walkley–Black method (Nelson and Sommers, 1982). Measured soil properties are given in Table 1. Soil temperatures were measured at depths of 10, 20, and 30 cm below the surface using soil temperature sensors during the entire period of study.

Model Parameterization, Performance Criteria, Sensitivity Analysis, and Calibration

Hourly rainfall, daily maximum and minimum air temperature, short-wave radiation, relative humidity, and wind speed were obtained from the Hamilton Airport, which is approximately 5 km from the studied site. Measured soil particle-size distribution, bulk density, particle density, and saturated hydraulic conductivity were used in the simulations. Parameters for the modified Brooks–Corey equations were obtained using a conversion method based on measured soil water retention data (Ma et al., 1999a). The fitted parameters include air-entry pressure, pore-size distribution index, saturated soil water content, and residual soil water content. These fitted parameters and measured K_s were then used to estimate parameters for the $K(h)$ curve using the capillary-bundle approach according to Campbell (1974). Water flux at the upper boundary was set equal to the current evaporation rate except during times of precipitation or irrigation for which recorded

hourly rainfall or irrigation rate was used. A unit-gradient bottom boundary was applied. Measured initial soil water content and soil temperature profiles were used in the simulations as initial conditions. Macropore flow was not simulated because little runoff was observed (nor was it simulated) during the entire period of the study. Soil microporosity was estimated as soil water content at 200-kPa suction on the water retention curve. An energy-balance procedure was used to estimate potential and actual evaporation (Ma et al., 1999b).

Pesticide degradation rate constants at different temperatures were obtained by fitting measured pesticide concentrations in the lab to first-order kinetics (Eq. [2]). These rate constants were then used to compute the activation energy. A similar procedure was used to obtain soil moisture adjustment factors (Eq. [3]). Model default depth-adjustment factors for degradation rate constant were used. Pesticide diffusion coefficient in soil solution was determined from pesticide diffusion coefficient in free water according to Boesten (1986). Pesticide equilibrium adsorption constant (K_d) was obtained from the equilibrium adsorption measurements, assuming linear adsorption. These values are shown in Table 2.

Measured soil-water content, soil temperature, and pesticide concentrations in the soil profile were compared with RZWQM simulations. A paired difference t test was used for comparing measured and simulated soil-water contents in the soil profile. For comparing pesticide concentrations in the soil profile, the criterion proposed by Parrish and Smith (1990) was used, which states that acceptable model predictions should be within a factor of two of the measured concentrations. The mass of pesticide in the soil was calculated from measured concentration and soil bulk density and was compared with model simulations to evaluate the performance of the model for simulating pesticide persistence. The normalized root mean square error (NRMSE) (Loague and Green, 1991) was used as a criterion for this evaluation:

$$\text{NRMSE} = \frac{100}{\bar{O}} \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}} \quad [5]$$

where O_i is the measured value and P_i is the corresponding predicted value; \bar{O} is the mean of the measured values, and n is the number of measurements. All statistical analyses were conducted at the 0.05 significance level.

RZWQM sensitivities of predicted persistence and leaching to major input parameters/variables were examined by varying each input parameter/variable at a time. Because a large number of input and output parameters/variables were used in the model, only sensitivities to predicted terbuthylazine total mass in the soil profile and its total concentration at 96-cm depth (the bottom of the simulated soil profile) were examined. The endpoints for determining the sensitivities of both pesticide

Table 1. Measured soil properties ($n = 6$) of Hamilton clay loam, Hamilton.†

Depth	Sand	Silt	Clay	OC	K_s	ρ	θ_{10}	θ_{wp}
m	%				cm h ⁻¹	Mg m ⁻³	m ³ m ⁻³	
0.0–0.10	26.0	45.0	29.0	4.6	25.4	1.13	0.46	0.21
0.10–0.20	23.0	41.0	36.0	0.8	2.6	1.23	0.38	0.20
0.20–0.30	14.0	49.0	37.0	0.8	2.1	1.25	0.38	0.26
0.30–0.45	15.0	37.0	48.0	0.7	1.1	1.33	0.43	0.36
0.45–0.75	6.0	13.0	81.0	0.5	1.1	1.02	0.60	0.51
0.75–1.20	4.0	17.0	79.0	0.2	1.1	0.94	0.63	0.52

† OC, soil organic C content; K_s , saturated hydraulic conductivity; ρ , soil bulk density; θ_{10} , soil water content at 10 kPa suction (field capacity); and θ_{wp} , soil water content at 1500 kPa suction (wilting point).

Table 2. Key pesticide parameter values for the Root Zone Water Quality Model.

Parameters	Acetochlor	Terbuthylazine
First-order rate constant (d^{-1}) at 22°C and 60% MWHC†	0.0356	0.0182
Degradation activation energy, $kJ\ mol^{-1}$	44.0	64.0
Walker's soil moisture correct factor	0.14	0.08
Linear equilibrium adsorption coefficient, $L\ kg^{-1}$	3.3	6.4
Optimized fraction of equilibrium sites (F)	0.96	0.96
Optimized kinetic sorption rate constant (EK_2), $L\ kg^{-1}$	0.132	0.256
Estimated reversible kinetic sorption rate constant (RK_2), h^{-1}	0.05	0.05

† MWHC, maximum water holding capacity.

mass and concentration predictions were at the end of the simulation. The input parameters/variables selected for sensitivity analysis are rainfall, maximum and minimum air temperatures, short-wave radiation, soil bulk density, microporosity, albedos of wet and dry soil, K_s , k , E_a , β , EK_2 , RK_2 , and K_d . The mean of the measured values or the best-estimated values from the literature were served as base values in the sensitivity analysis. The range of parameter variation was determined primarily based on the sensitivity of the parameter. If a selected parameter has multiple values (e.g., K_s has six values, one for each soil horizon) then all the values were varied simultaneously by the same percentage about the base value. A model parameter/variable is defined as sensitive if changes in that parameter/variable result in changes in output variables as large or larger than the parameter changes (Lane and Ferreira, 1980). We further defined the sensitivity index for parameter/variable i (S_i) as:

$$S_i = \left(\frac{P_i - P_i^b}{P_i^b} \right) 100\% \quad [6]$$

where P_i is the prediction with varying parameter/variable i and P_i^b is the same prediction with the corresponding base value.

Model calibration was performed manually by tuning each sensitive parameter individually starting with the most sensitive parameter and then comparing model performance using the above statistics. This approach of model calibration does not account for the effect of simultaneous change of parameters on model predictions, which can result in better fit than individual change of parameters. Because RZWQM least satisfactorily simulated pesticide concentration distributions in the soil profile in uncalibrated mode, the calibration was focused on pesticide partitioning process in the soil. The range of parameter values for tuning was 50% above and below the basis value used in the sensitivity analysis. Model calibration was also used to obtain pesticide kinetic sorption parameters when the E-K sorption model was used. For this purpose, we calibrated the model by minimizing the root mean square error between measured and simulated pesticide mass at low application rate and then examined whether or not the calibrated model improved the predictions of the measured data at high application rate. Again, the same statistics were used to evaluate model performance.

RESULTS AND DISCUSSION

Measured and Simulated Soil Temperature and Soil Water Content Distributions

Data in Fig. 2 show selected comparisons between measured and RZWQM-predicted soil water content distributions over the entire period of the study of 476 d.

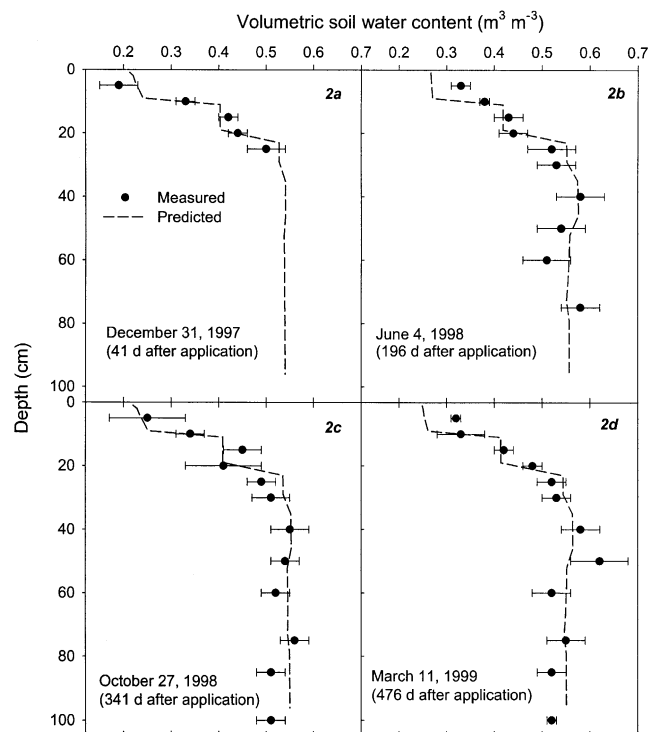


Fig. 2. Measured and RZWQM-predicted soil water content distributions in the soil profile of a Hamilton clay loam.

We selected soil water content distributions representing typical field conditions in four seasons for comparisons. The soil water content distribution on 31 Dec. 1997 (Fig. 2a) represents that in summer when rainfall is intense but infrequent. This is usually the water-deficient season because of high evaporation demand. The soil water content on 4 June 1998 (Fig. 2b) represents that in winter when rainfall is frequent and evaporation is low because of low temperature and solar radiation. Rainfall excess often occurs in this season. Runoff rarely occurs during winter, however, because of high water holding capacity of the soil. The soil water content on 27 Oct. 1998 (Fig. 2c) represents that in spring when rainfall is light but frequent and evaporation is relatively high because of high solar radiation. The soil water content on 11 Mar. 1999 (Fig. 2d) represents that in autumn when rainfall is light and infrequent; this is usually the dry season.

Sampling immediately after a significant rainfall or long after a dry period was avoided. Therefore, these data generally represented soil water contents between wilting point (1500-kPa suction) and field capacity (10-kPa suction). Nevertheless, these measurements reflected the influences of constant water evaporation and redistribution on soil water contents under transient field conditions.

The ratio of predicted/measured soil water contents at all depths varied between 0.8 and 1.1, with an average of 1.0. A linear regression analysis between measured and predicted soil water contents resulted in an adjusted regression coefficient $r^2 = 0.89$, with the slope of the regression line (1.04) not significantly different from 1.0 and the intercept (-0.02) not significantly different from

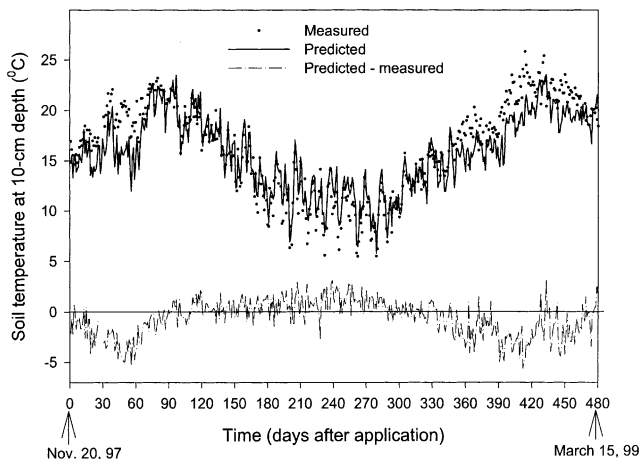


Fig. 3. Measured and RZWQM-predicted soil temperature at 10-cm depth from 1997 to 1999.

0.0. A paired-difference t test for all measured and predicted soil water contents in the soil profile also showed that there was no significant difference between measured and predicted values ($p > 0.84$).

The implications of these results cannot be overlooked because accurate simulation of soil water content distribution [$\theta(z, t)$] is critical for simulating solute transport. Although $\theta(z, t)$ is not directly used to estimate solute flux, it is used to calculate water flux from which solute flux is calculated. Because $\theta(h)$ is known for each soil horizon, $K(h)$ can be derived using the capillary bundle model (Campbell, 1974) and the matric potential distributions [$h(z, t)$] can also be calculated from $\theta(z, t)$. Given that the sink term in Eq. [1] is zero (no plant root uptake and no tile drain), soil water flux can then be calculated from the knowledge of $\theta(z, t)$. Thus, good estimate of $\theta(z, t)$ provides the basis for simulating solute transport. The agreement between predicted and the average measured soil water content distributions in the field further suggests that, on average, the lab-measured $\theta(h)$ data and the derived $K(h)$ curve from the $\theta(h)$ data reasonably described soil water content distributions in the field.

Soil moisture and temperature are among the key factors that influence pesticide degradation (Walker et al., 1996). Examinations of RZWQM simulations for soil temperature at 10-, 20-, and 30-cm depths showed that the measured and simulated soil temperatures were highly correlated, with an adjusted regression coefficient $r^2 > 0.81$. Only soil temperatures at 10-cm depth are shown (Fig. 3) because the pesticides did not leach below this depth. Simulated soil temperature was generally within 5°C of the measured soil temperature, most within 3°C (Fig. 3). However, there appears a general pattern that RZWQM underestimated soil temperature during the summer months (December through March) when temperature was the highest and overestimated it in winter (June through August) when temperature was the lowest (Fig. 3).

Measured and Simulated Acetochlor and Terbutylazine Dissipation in the Field

Concentrations of acetochlor in the field soil were below the detection limit ($40 \mu\text{g kg}^{-1}$) at all depths

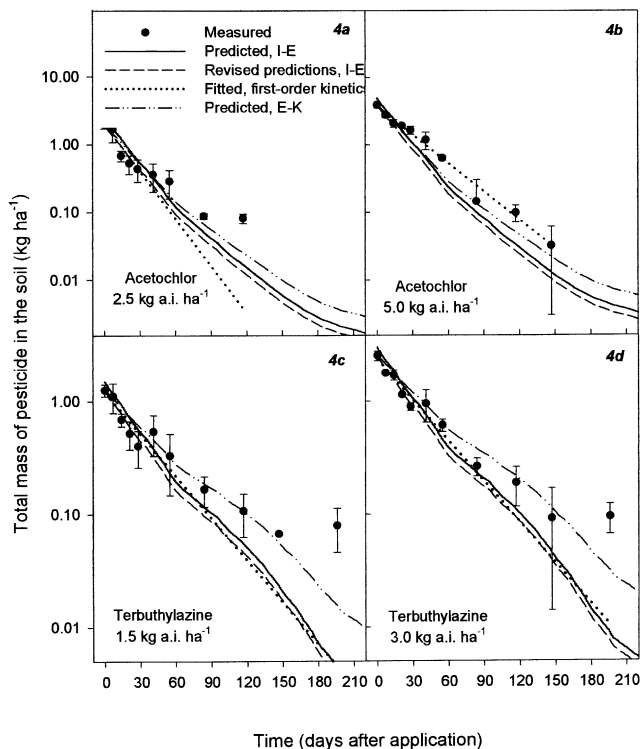


Fig. 4. Measured and RZWQM-predicted persistence of acetochlor and terbutylazine in the field. Predictions were performed using a linear instantaneous equilibrium (I-E) partitioning model with projected application rates and measured amounts on the day of application as initial amounts (revised predictions) and a two-site, equilibrium-kinetic (E-K) sorption model with optimized kinetic parameters. Fitting first-order kinetics to the measured data was also included.

at 147 and 196 d after applications at low and high application rates, respectively; while concentrations of terbutylazine in the soil were below the detection limit ($15 \mu\text{g kg}^{-1}$) at 288 d after applications at both application rates. Visual examinations of the measured data showed that dissipation of both pesticides in the field at both application rates generally followed exponential decay (Fig. 4). Fitting the measured data to first-order kinetics (Eq. [2]) produced regression coefficients $r^2 > 0.91$. The resulting dissipation half-life was 16 d for acetochlor and 25 d for terbutylazine when averaged for both application rates. However, the fitted curve overestimated pesticide mass initially and underpredicted it later (Fig. 4), indicating that dissipation of the pesticides in the field did not exactly follow first-order kinetics. In fact, analyses of the measured data suggest an initial rapid and later slow dissipation pattern. This biphasic dissipation is better described by a more complex, variable rate dissipation model than a constant rate first-order kinetics (Reyes and Zimdahl, 1989; Ma et al., 2004).

Data in Fig. 4 show that the total mass of the pesticides in the soil was barely dissipated for an extended period of time (from 30 to 49 d) between the last two sampling dates (Fig. 4). This suggests that the pesticides might be strongly bounded to the soil and protected from degradation, or that larger measurement errors might be involved at later sampling dates when pesticide con-

centrations were low (Fig. 4). Note that the dissipation pattern was broken at 41 d after application for both pesticides at both application rates (Fig. 4). This was the time when the sampling instrument was changed from stainless steel tube to Humax sampler. Thus, this abrupt change in pesticide dissipation rate could be caused by changes in sampling instruments. It could also be caused by other factors as discussed by Ma et al. (2004). For example, the pesticides could have moved deeper into the soil profile before 41 d after application, avoiding intense interactions with soil surface processes that accelerated pesticide degradation. Increased pesticide adsorption to the soil with time could also change pesticide degradation rate.

Data in Fig. 4 also show measured and RZWQM-predicted total masses of acetochlor and terbuthylazine in the soil. The predictions were performed using site-specific soil and weather data and first-order degradation rate constants derived from the lab incubation studies at a range of temperatures and soil water contents (Table 2). It appears that the predicted pesticide residue dynamics (persistence) match those measured in the field, although the model overpredicted the persistence initially and significantly underpredicted it later (Fig. 4). As analyzed previously, large uncertainties in measurements and conceptualization might be involved at low concentrations, which lead to these discrepancies. Although RZWQM updated the first-order rate constant daily based on changing soil and environmental conditions, the nature of first-order kinetics makes it difficult to describe the biphasic dissipation observed in the field. Presumably incorporation of a biphasic or a two-compartment dissipation model such as that proposed by Reyes and Zimdahl (1989) could improve RZWQM predictions of these field observations.

The NRMSE between measured and predicted masses were 41 and 35% for acetochlor and 37 and 36% for terbuthylazine at low and high application rates, respectively. This compares well with the coefficient of variation of the measurements, which varied between 9 and 45%. Therefore, the model prediction errors were within the field measurement errors.

The above simulations assumed that the mass of the pesticides reaching the soil on the day of application was the projected application amount, as is normally assumed in model applications. However, the measured mass at 3 h after application was noticeably smaller than the projected amount for both pesticides, suggesting that some amounts of the applied pesticides were lost during and shortly after applications, presumably through drift and volatilization losses. These losses may explain the initial overpredictions of total pesticide mass in the soil (Fig. 4).

When the measured amounts were used as the initial amounts in model simulations, RZWQM better predicted the persistence of both pesticides in the soil, overall, although the model still noticeably underpredicted the pesticide persistence later in the study (Fig. 4). This may be the limitation of the model with first-order kinetics for pesticide dissipation and the instantaneous equilibrium assumption for pesticide adsorption. These pre-

dictions are denoted as 'revised predictions' in Fig. 4 to differentiate those with the projected application rates as initial amounts. With these revisions, the resulting NRMSE values were 29 and 39% for acetochlor, and 32 and 16% for terbuthylazine at low and high application rates, respectively. The relatively larger errors for acetochlor predictions might result from the degradation rate constants that were derived from a study in a different soil. These results demonstrate that overall RZWQM reasonably predicted persistence of both pesticides in the field using parameters primarily derived from the lab studies without further model calibration. However, model sensitivity analysis and calibration were conducted, as detailed below, to examine whether or not calibration of sensitive parameters can significantly improve RZWQM predictions.

Measured and RZWQM-Simulated Pesticide Concentrations in the Soil Profile

Relatively low concentrations of the pesticides were measured below 5 cm and none were measured below 10 cm during the entire period of the study, indicating that macropore flow and preferential flow, if any, did not contribute significantly to pesticide transport in the soil profile. High organic matter content in surface soil layer (Table 1) retained pesticides and prevented leaching to greater depths. High clay and silt contents in the soil might also retard the pesticides. Note that Hamilton clay loam is a highly structured soil and surface cracks were observed during the study. Thus, there is a possibility that the pesticides could have transported to depths deeper than 10 cm through surface cracks and other preferential paths early in the study, and then dissipated before the next sampling event. Since we did not collect samples below 10 cm before Day 41 after application, we are unable to verify this hypothesis. Soil samples were not collected at deeper depths early in the study because we did not expect these two pesticides to move below 10 cm based on previous studies of pesticide leaching in this soil (Muller et al., 2003). The low detection limits of the HPLC methods for both pesticides may also lead to trace amount of the pesticides undetected at deeper depths.

Data in Fig. 5 show the measured and predicted acetochlor and terbuthylazine concentrations in the soil profile at low application rates. Similar results were obtained at high application rates and thus were not shown. The predictions were performed using the measured amounts at 3 h after application as the initial amounts. At 28-d after acetochlor application (Fig. 5a), the depth-weighted average concentrations predicted by RZWQM were 1.1 and 0.7 times the corresponding measured concentrations for both 0- to 5- and 5- to 10-cm depths, respectively. However, the predicted concentrations at 117-d after acetochlor application (the last measured data point on the dissipation curve of Fig. 4a) were approximately 12% of the measured concentrations for both depths (Fig. 5b). Likewise, the predicted terbuthylazine concentrations at 84 d after application were within a factor of two of the measured concentrations

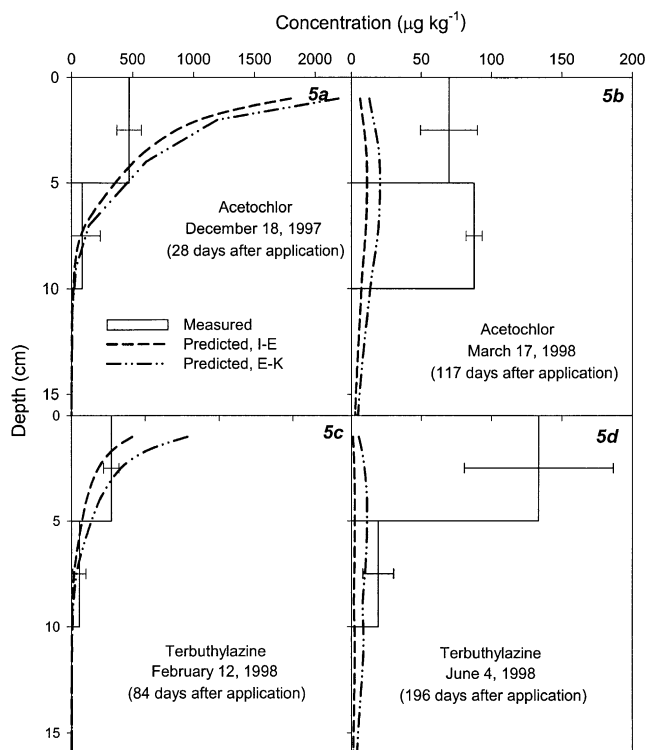


Fig. 5. Measured and RZWQM-predicted acetochlor and terbuthylazine concentrations in the soil profile at 2.5 and 1.5 kg a.i. ha⁻¹ rate, respectively. Predictions were performed using a linear instantaneous equilibrium (I-E) partitioning model with measured amounts on the day of application as initial amounts and a two-site, equilibrium-kinetic (E-K) sorption model with optimized kinetic parameters.

for both depths (Fig. 5c). But the predicted concentrations at 196 d after application were approximately 1 and 12% of the measured concentrations for 0- to 5- and 5- to 10-cm depths, respectively (Fig. 5d).

Better predictions of the pesticide concentrations in the soil profile were observed between 0 and 55 d after application for acetochlor and between 0 and 119 d after application for terbuthylazine. The predictions deviated more and more from the measurements with time thereafter. This is coincided with the pesticide mass predictions and is likely to be a result of underpredictions of pesticide mass in the soil profile later in the study (Fig. 4). Poor predictions of the pesticide concentrations at later sampling dates could also result from increased pesticide adsorption to the soil, which could cause decreases in pesticide degradation rate. This is explored later. Although RZWQM did not precisely predict the measured concentrations in value later in the study, it predicted the trends of concentration distributions of both pesticides in the soil profile.

When evaluated over all data points for both pesticides at both application rates and depths, which consist of 110 values, RZWQM initially overestimated acetochlor and terbuthylazine concentrations in the soil profile and later underestimated the concentrations. Applying the 'within 2X' criterion (Parrish and Smith, 1990) to all data, 68 and 35% of the predicted concentrations were within a factor of two of the measured concentrations for 0- to 5- and 5- to 10-cm depths, respectively. These are predictions based on the linear I-E adsorption assumption using key parameters primarily derived from lab studies without model calibration.

Calibrations of sensitive model parameters could improve the pesticide mass and concentration predictions later in the study. Of the major input parameters/variables analyzed for sensitivity to terbuthylazine mass and concentration predictions, soil bulk density, solar radiation, rainfall, air temperature, pesticide equilibrium adsorption constant, half-life, activation energy, and kinetic sorption rate constant were identified as sensitive parameters/variables (Table 3) according to the crite-

Table 3. Sensitivities of predicted terbuthylazine mass in the soil profile and concentrations at 96-cm depth at the end of the simulation to various input parameters/variables.

Parameters	Base value	Variation	Sensitivity index [†]	
			Mass	Concentration
			%	
Bulk density	Table 1	10	-13.2	53.7
		-10	16.1	123.4
Equilibrium adsorption coefficient	6.4	25	-31.1	-81.7
		-25	45.3	478.7
Half-life	38	10	-57.1	-57.5
		-10	104.2	103.5
Saturated hydraulic conductivity	Table 1	25	-0.1	3.3
		-25	-2.0	-11.1
Solar radiation	Measured	10	-4.9	-15.5
		-10	5.7	20.0
Rainfall	Measured	10	31.1	195.5
		-10	-26.5	-75.7
Air temperature	Measured	+5	-41.6	-39.2
		-5	68.3	61.9
Activation energy	64	25	197.5	197.9
		-25	-71.0	-73.0
Walker's β	0.082	25	-4.8	-2.1
		-25	5.0	2.0
Kinetic sorption rate constant EK ₂	0.256	10	21.1	20.3
		-10	-17.8	-16.7
Reversible kinetic sorption rate constant RK ₂	0.05	50	-0.5	-2.7
		-50	0.9	4.5

[†] The sensitivity index is the relative change (percentage) of predictions from a varying input parameter/variable to a base parameter/variable, as described by Eq. [6].

tion by Lane and Ferreira (1980). Varying each of these parameters individually within a range of values using the I-E adsorption model did not significantly improve the overall predictions of pesticide mass and concentrations in the soil profile, suggesting that the I-E adsorption assumption may be invalid for this system.

Increased pesticide sorption to the soil with time could significantly affect pesticide fate and transport predictions, especially long after application (Boesten, 1986). This process could also affect the pesticide mass and concentration predictions later in this study. The I-E adsorption model assumes a constant partitioning rate, therefore, it is not capable of simulating increased pesticide sorption to the soil with time, while the two-site E-K sorption model has this capability. To test this hypothesis and to further explore the capability of RZWQM for simulating time-dependent sorption of pesticides in the soil, we run RZWQM with the E-K sorption model. Predictions of pesticide mass and concentrations at high application rate were improved (Fig. 4) using the E-K sorption model, with the optimized kinetic parameters (Table 2) obtained by minimizing the difference between measured and simulated pesticide mass at low application rate. These predictions were also included in Fig. 4 for comparison with those predicted using the I-E adsorption model. The NRMSE values between measured and predicted total mass in the soil profile were 27 and 22% for acetochlor, and 22 and 16% for terbuthylazine at low and high application rates, respectively. Of the 110 data, 88 and 41% of the predicted concentrations were within a factor of two of the measured concentrations for 0- to 5- and 5- to 10-cm depths, respectively. Therefore, application of a time-dependent pesticide sorption model is the key to successful predictions of pesticide mass and concentration in the soil.

CONCLUSIONS

Dissipation of acetochlor and terbuthylazine residues in this high organic matter content, clay loam soil followed pseudo first-order kinetics (adjusted $r^2 > 0.91$). The field dissipation half-life was 16 d for acetochlor and 25 d for terbuthylazine. High organic matter content in the topsoil horizon (0–10 cm) retained the pesticides from leaching below the 10-cm depth. RZWQM reasonably predicted soil water content distributions in the soil profile in the field using parameters primarily derived from controlled lab studies. RZWQM also reasonably predicted persistence of both pesticides in the field using the linear instantaneous equilibrium adsorption model by integrating the key parameters measured in the lab with measured environmental variables, although it tended to underpredict pesticide persistence long after application. RZWQM better simulated pesticide mass and concentration long after application using a two-site E-K sorption model. Application of a time-dependent pesticide sorption model was the key to successful predictions of pesticide mass and concentration in the soil.

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